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## TEMPERATURE RELAXATION OF A HIGHLY RARIFIED GAS

V. V. Andreyev, I. F. Mikhaylov, L. V. Tanatarov

ABSTRACT. The problem of establishing the thermal relaxation of a rarified gas in a closed volume, the surface temperature distribution being nonuniform, is discussed. The dependence of temperature on spatial coordinates and time is preset. Reflection of particles from the boundary is taken as diffusive. The possibility of particle adsorption is considered, and the particle distribution function for a long time interval is obtained.

Introduction

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The operating principle of adsorption and condensation vacuum pumps, as we know, is one of reducing the volume of particles in the evacuated volume during the cooling of the condensing element as the particles are adsorbed on the cool surface. The development of a theory for pumps such as these requires consideration of the simplest model that can be investigated mathematically. That model is an expanse holding a rarified gas. The temperature of walls capable of adsorbing gas particles is a specified function of coordinates and time. This model can be used to find the gas distribution function in terms of velocities and coordinates, to ascertain the influence of spatial nonuniformity wall temperature, and to establish the time required for the gas to reach equilibrium when there is a sharp change in the gas (temperature relaxation). Since, under real conditions, only the temperature of that part of the surface limiting the gas changes (the cooled surface of a condensation pump, for example), it is of interest to ascertain the time of temperature relaxation in terms of the ratio of the area of this part to the entire area of the vacuum chamber surface.

A real pump has a macroscopic flow, the result of the inflow, caused by the discharge in the previous stage. Moreover, always to be dealt with is a mixture of a great many different residual gases, oil vapors, and the like. All of this serves to greatly complicate the mathematical consideration of the pro-

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\* Numbers in the margin indicate pagination in the foreign text.

blem. This paper does not intend to deal with all the factors influencing the evacuation process, but rather to investigate only the exhausting action of the cooled surface, because this is the basis of the operating principle of condensation and adsorption pumps alike.

### 1. Statement of the Problem

Let us consider a gas contained in a volume limited by a closed, convex surface of arbitrary shape, for which there is given some temperature distribution that depends on coordinates and on time. The gas will be taken as rarefied to the point that  $l \gg L$  ( $l$  is the mean free path for the particles,  $L$  is the characteristic dimension of the expanse). Let us seek the particle distribution function in terms of coordinates and pulses. This function,  $F(\vec{r}, \vec{p}, t)$ , will be satisfied by the kinetic equation

$$\frac{\partial F}{\partial t} + \frac{1}{m} (\vec{p} \nabla_{\vec{r}}) F(\vec{r}, \vec{p}, t) = 0. \quad (1)$$

Let us suppose no external fields are acting on the molecules of gas. In such case the left side of Eq. (1) will have no summand proportional to  $\vec{p}$ . The condition  $l \gg L$  results in the integral of collisions equalling zero. Let us designate the temperature of the surface of the expanse at point  $\vec{r}$  at time  $t$  by  $T(\vec{r}, t)$ . It is apparent that Eq. (1), by itself, will not solve the problem. It still is necessary to write the boundary condition describing the mechanism whereby the gas particles are reflected from the wall. We will take it that the particles hitting the surface are "thermalized" before they leave it. In other words, the distribution of the particles flying off the surface is isotropic in direction, and their distribution function is in the form

$$F_0 = A e^{-\frac{p^2}{2mkT(\vec{r}, t)}}, \quad (\vec{p} \vec{n}) < 0. \quad (2)$$

Here  $A$  does not depend on pulses, and  $\vec{n}$  is an external normal to the surface at point  $\vec{r}$ .

It is convenient to write the preexponential factor  $A$  in Eq. (2) in the form

$$A = \frac{2m}{\pi} \frac{n(\vec{r}, t)}{[2mkT(\vec{r}, t)]^2}, \quad (3)$$

where

$n(\vec{r}, t)$  is a function subject to determination.

The system of Eq. (1) characteristics is in the form

$$\vec{r} = \vec{r}' + \frac{\vec{p}}{m} \tau,$$

where

$\vec{r}$  is the point of observation;

$\vec{r}'$  is that point on the surface off which a particle with pulse  $\vec{p}$ , observed at point  $\vec{r}$ , flies;

$\tau$  is the time of flight for this particle from point  $\vec{r}'$  to point  $\vec{r}$ .

Obviously

$$\tau = \frac{m}{p} |\vec{r} - \vec{r}'|. \quad (4)$$

The solution of Eq. (1) satisfying the condition of Eq. (2) on the surface of the expanse is

$$F(\vec{r}, t; \vec{p}) = F_0(\vec{r}', t - \tau; \vec{p}). \quad (5)$$

Let us write the normal component of the flow,  $J_n$ , at the wall as

$$mJ_n = \int_{(\vec{p} \cdot \vec{n}) > 0} (\vec{p} \cdot \vec{n}) d\vec{p} F_0(\vec{r}', t - \tau; \vec{p}) + \int_{(\vec{p} \cdot \vec{n}) < 0} (\vec{p} \cdot \vec{n}) d\vec{p} F_0(\vec{r}, t; \vec{p}). \quad (6)$$

Utilizing Eqs. (2) and (3), and integrating, we find

$$J_n = -n(\vec{r}, t) + \frac{2}{\pi} \int_{(\vec{p}n) > 0} (\vec{p}n) d\vec{p} \frac{n(\vec{r}', t - \tau)}{[2mkT(\vec{r}', t - \tau)]^2} e^{-\frac{p^2}{2mkT(\vec{r}', t - \tau)}}.$$

As we see,  $n(\vec{r}, t)$  is equal to the flow of particles from the surface inside the volume upon selection of normalization established by Eq. (3). /723

In the steady-state case,  $T(\vec{r}, t)$  does not depend on  $t$ , and  $J_n = 0$ , and this leads to the following integral equation for finding the unknown function  $n(\vec{r})$

$$n(\vec{r}) = \frac{2}{\pi} \int_{(\vec{p}n) > 0} (\vec{p}n) d\vec{p} \frac{n(\vec{r}')}{[2mkT(\vec{r}')]^2} e^{-\frac{p^2}{2mkT(\vec{r}')}}.$$

Introducing spherical coordinates and directing the  $Z$  axis with respect to  $\vec{n}$ , we obtain

$$p_z = p \cos \vartheta; \quad p_x = p \sin \vartheta \cos \varphi; \quad p_y = p \sin \vartheta \sin \varphi.$$

After integrating with respect to  $p$  from 0 to  $\infty$ , the equation will take the form

$$n(\vec{r}) = \frac{1}{\pi} \int_0^{\frac{\pi}{2}} \sin \vartheta \cos \vartheta d\vartheta \int_0^{2\pi} d\varphi n(\vec{r}').$$

Its solution is a constant

$$n(\vec{r}) = \text{const.} \quad (7)$$

We conclude that in the steady-state case the flow of particles from the surface inside the volume is a constant magnitude for all points of the surface. This result was the one obtained in reference [1].

## 2. Adsorption in the nonsteady-state case

Pointed out in the preceding section was the fact that in the steady-state case  $n(\vec{r}, t) = \text{constant}$ . This is not so in the nonsteady-state case.

We will assume that all gas particles striking the surface are adsorbed (the reflectance equals zero). The flow of particles desorbing reversibly inside the volume equals  $n(\vec{r}, t)$ . (We are talking about particles deposited on the surface some time previously. They have been thermalized and now are being desorbed). This flow is proportional to the number of particles on the surface, that is, to the magnitude

$$\int_{-\infty}^t J_n(\vec{r}, t') dt'$$

The following relationship can be written

$$n(\vec{r}, t) = \frac{1}{\tau_0} e^{-\frac{U}{kT(\vec{r}, t)}} \int_{-\infty}^t J_n(\vec{r}, t') dt', \quad (8)$$

$\tau_0$  is the magnitude of the order of the period of oscillations of an atom in the lattice ( $\tau_0 \sim 10^{-13} \text{ sec}^{-1}$ );

$U$  is the energy required for a gas particle to escape from the surface.

Strictly speaking, the condition set forth in Eq. (8) is correct only when no more than one layer of particles is adsorbed on the surface. If the entire surface is completely covered by a monolayer of adsorbed particles,  $n(\vec{r}, t)$  ceases to depend on their number, so the condition set forth in Eq. (8) should be written

$$n(\vec{r}, t) = \frac{a}{\tau_0} e^{-\frac{U}{kT(\vec{r}, t)}} \Phi \left( \int_{-\infty}^t J_n(\vec{r}, t') dt' \right), \quad (9)$$

where

$\Phi(x)$  is a function linear for small  $x$ , and approaching 1 asymptotically

when  $x \rightarrow \infty$

$$\Phi(x) = \begin{cases} x, & x \ll 1, \\ I, & x \gg 1, \end{cases} \quad (10)$$

where

$a, I$  are constants.

Let us assume that the number of adsorbed atoms is small, and that we can use Eq. (8). The distribution function for the particles flying off the surface will be sought for in the form shown in Eqs. (2) and (3). Eq. (5) will yield the distribution function for the particles inside the volume.

Substituting the Eq. (2) distribution function in Eq. (8), we obtain the equation for finding the unknown function  $n(\vec{r}, t)$

$$n(\vec{r}, t) = \frac{1}{\tau_0} e^{-\frac{U}{kT(\vec{r}, t)}} \int_{-\infty}^t dt' \left\{ \frac{2}{\pi} \int_{(\vec{p} \cdot \vec{n}) > 0} \vec{p} n d\vec{p} \times \right. \\ \left. \times \frac{n(\vec{r}', t' - \tau) e^{-\frac{p^2}{2mkT(\vec{r}', t' - \tau)}}}{[2mkT(\vec{r}', t' - \tau)]^2} - n(\vec{r}, t') \right\}.$$

This general statement of the problem is extremely complex, so we shall consider its simplest variant. Let us take it that the surface temperature is a function of time only, and that the surface proper is a sphere. Let us hypothecate the following temperature time dependency

$$T(t) = \begin{cases} T_-, & t < 0, \\ T_+, & t > 0. \end{cases} \quad (11)$$

Let us select the original condition as

$$n(t) = n_-, \quad t < 0.$$

Because the temperature changes in bounds [according to Eq. (11)] the function

$$f(T) = \frac{1}{\tau_0} e^{-\frac{U}{kT}},$$

which is the probability of desorption of the particle, too will change in bounds. Then, as follows from Eq. (8)

$$n_- = f(T_-) \int_{-\infty}^0 J_n(t') dt'.$$

And when  $t > 0$

$$n(t) = \frac{f(T_+)}{f(T_-)} n_- + f(T_+) \int_0^t J_n(t') dt'. \quad (12)$$

Let us set the origin of the spherical system of coordinate at the point of observation,  $\vec{r}$ . Then, from this point on the surface of the sphere

$$\tau = \frac{2Rm \cos \vartheta}{\rho}, \quad |\vec{r} - \vec{r}'| = 2R \cos \vartheta.$$

We obtain the following expression

$$J_n(t) = -n(t) + \frac{4}{t_+^2} \int_0^t n(t-t') t' dt' \int_0^{t_+/t} z^5 dz e^{-z^2} + \\ + 2n_- \int_0^{t_-/t} z^3 e^{-z^2} \left(1 - z^2 \frac{t_-^2}{t_-^2}\right) dz,$$



for the flow  $J_n(t)$ , where

$$t_{\pm}^2 = \frac{2R^2 m}{kT_{\pm}}. \quad (13)$$

Applying a one-sided Laplace transform to both sides of Eq. (12), and using the expression written for  $J_n(t)$ , we obtain

$$n(s) = \frac{n_-}{s} \frac{\frac{1}{f(T_-)} + 2 \int_0^{\infty} e^{-st} dt \int_0^{t_-/t} z^3 e^{-z^2} \left(1 - z^2 \frac{t_-^2}{t^2}\right) dz}{\frac{1}{f(T_+)} + 2 \int_0^{\infty} e^{-st} dt \int_0^{t_+/t} z^3 e^{-z^2} \left(1 - z^2 \frac{t_+^2}{t^2}\right) dz}.$$

Applying the inverse transform we find

$$n(t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} n(s) e^{st} ds. \quad (14)$$

Readily seen is that

$$\int_0^{\infty} e^{-st} dt \int_0^{t_-/t} z^3 e^{-z^2} \left(1 - z^2 \frac{t_-^2}{t^2}\right) dz = t_- F(st_-),$$

$$F(x) = \int_0^{\infty} e^{-xy} dy \int_0^{1/y} z^3 e^{-z^2} (1 - z^2 y^2) dz.$$

We are interested in the asymptotic behavior of  $n(t)$  for large  $t$ . We must know the behavior of the function  $n(s)$  near zero [ $n(s)$  is a form of the Laplace function  $n(t)$ ]. It can be shown that this expansion also has the form

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$$n(s) = \frac{n_- \frac{1}{f(T_-)} + \frac{\sqrt{\pi}}{3} t_- + \dots - t_-^4 \frac{1}{16} s^3 \ln s}{\frac{1}{f(T_+)} + \frac{\sqrt{\pi}}{3} t_+ + \dots - t_+^4 \frac{1}{16} s^3 \ln s} \quad (15)$$

Substituting Eq. (15) in Eq. (14), and integrating

$$n(t) = n_- \frac{\frac{3}{f(T_-)} + \sqrt{\pi} t_-}{\frac{3}{f(T_+)} + \sqrt{\pi} t_+} + \frac{n_-}{18t^3 (1/f(T_+) + t_+ \sqrt{\pi}/3)} \times \\ \times \left\{ t_-^4 - t_+^4 \frac{1/f(T_-) + t_- \sqrt{\pi}/3}{1/f(T_+) + t_+ \sqrt{\pi}/3} \right\}$$

or, using Eq. (13)

$$n(t) = n_- \frac{3\tau_0 e^{U/kT_-} + R \sqrt{\frac{2\pi m}{kT_-}}}{3\tau_0 e^{U/kT_+} + R \sqrt{\frac{2\pi m}{kT_+}}} \left\{ 1 + \frac{2R^4 m^2}{3t^3 (3\tau_0 e^{U/kT_-} + R \sqrt{\frac{2\pi m}{kT_-}})} \times \right. \\ \times \left. \left[ \frac{1}{(kT_-)^2} - \frac{1}{(kT_+)^2} \frac{3\tau_0 e^{U/kT_-} + R \sqrt{\frac{2\pi m}{kT_-}}}{3\tau_0 e^{U/kT_+} + R \sqrt{\frac{2\pi m}{kT_+}}} \right] \right\} \quad (16)$$

When adsorption does not occur, Eq. (16) yields

$$n(t) \approx \sqrt{\lambda} n_- \left\{ 1 + \frac{2R^3 m^2 (1 - \lambda^{-3/2})}{3t^3 \sqrt{2\pi} (kT_-)^{3/2}} \right\}, \quad \lambda = \frac{T_+}{T_-}$$

if we set  $\tau_0 = 0$ .

The asymptotic form of the function  $n(t)$  for small  $t$  is

$$n(t) \approx \frac{f(T_+)}{f(T_-)} n_- + f(T_+) n_- t \left( 1 - \frac{f(T_+)}{f(T_-)} \right).$$

The Eq. (9) condition must be used if there is a thick layer of gas molecules on the surface of the expanse (a film of condensate). We shall take it that the layer of adhesive particles is so thick that the lower relationship of Eq. (10) is applicable to Eq. (9). Then

$$n(\vec{r}, t) = \frac{Ia}{\tau_0} e^{-\frac{U}{kT}}.$$

Let us now use this expression to find  $J_n$ . Then

$$\frac{\tau_0 J_n}{Ia} = -e^{-\frac{U}{kT_+}} + \frac{2}{\pi} \int d\vec{\Omega} (\vec{\Omega} n) \left\{ \int_0^{\frac{|\vec{r}-\vec{r}'| m}{t}} p^3 dp e^{-\frac{p^2 + 2mU}{2mkT_-}} + \right.$$

$$\left. + \int_{\frac{|\vec{r}-\vec{r}'| m}{t}}^{\infty} p^3 dp e^{-\frac{p^2 + 2mU}{2mkT_+}} \right\}.$$

The expression obtained is valid for an expanse of any shape. Integrating with respect to  $p$ , we obtain

$$\begin{aligned} \frac{\tau_0 J_n}{Ia} = & \frac{1}{\pi} \int d\vec{\Omega} (\vec{\Omega} n) \left\{ e^{-\frac{U}{kT_-}} \left[ 1 - \left( 1 + \frac{|\vec{r}-\vec{r}'|^2 m}{2kT_- t^2} \right) e^{-\frac{|\vec{r}-\vec{r}'|^2 m}{2kT_- t^2}} \right] - \right. \\ & \left. - e^{-\frac{U}{kT_+}} \left[ 1 - \left( 1 + \frac{|\vec{r}-\vec{r}'|^2 m}{2kT_+ t^2} \right) e^{-\frac{|\vec{r}-\vec{r}'|^2 m}{2kT_+ t^2}} \right] \right\}. \end{aligned}$$

If  $L_m^2/kT_+t^2 \ll 1$ , the exponents containing  $|\vec{r} - \vec{r}'|^2$  can be expanded in series and

$$J_n = \frac{m^2 I a}{4\pi t^4 \tau_0} \left( \frac{e^{-U/kT_-}}{(kT_-)^2} - \frac{e^{-U/kT_+}}{(kT_+)^2} \right) \int d\vec{\Omega} (\vec{\Omega} n) |\vec{r} - \vec{r}'|^4.$$

### 3. Nonuniform Distribution of Temperature on the Surface in the Nonsteady-state case

The preceding section assumed a bound-like change in temperature taking place simultaneously over the entire surface. Now we shall assume that it takes place only over a part of that surface. In other words, before time  $t = 0$  the temperature of the entire surface is equal to  $T_-$ , and at time  $t = 0$  the temperature of part  $S_1$  of the surface will equal  $T_+$ , and will then remain so. Moreover, we shall take it that at  $t = 0$  quite a thick layer of gas particles already has condensed on the surface such that the flow of particles evaporating from that surface will depend solely on the temperature, or

$$n_- = A e^{-U/kT_-},$$

where  $A$  is a constant.

The flow  $J_n^-$  over that part of the surface where the temperature remains equal to  $T_-$ , even when  $t > 0$ , is

$$\begin{aligned} J_n^- = & -n_-(\vec{r}, t) + \frac{2}{\pi} \int d\vec{\Omega} (\vec{\Omega} n) \int_0^\infty \frac{p^3 dp}{(2mkT_-)^2} e^{-\frac{p^2}{2mkT_-}} n_-(\vec{r}', t - \tau) + \\ & + \frac{2}{\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \int_0^{\frac{|\vec{r} - \vec{r}'|}{t} m} \frac{p^3 dp}{(2mkT_-)^2} e^{-\frac{p^2}{2mkT_-}} n_-(\vec{r}', t - \tau) + \\ & + \frac{2}{\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \int_{\frac{|\vec{r} - \vec{r}'|}{t} m}^\infty \frac{p^3 dp}{(2mkT_+)^2} e^{-\frac{p^2}{2mkT_+}} n_+(\vec{r}', t - \tau), \end{aligned}$$

where

$n_{\pm}(\vec{r}', t - \tau) = A e^{-\frac{U}{kT_{\pm}}}$ ,  $\Omega(\vec{r})$  is the solid angle corresponding to that part of the surface,  $S_1$ , the temperature of which is changing, and the lines containing the integral signify integration with respect to the remainder of the surface.

The expression for  $J_n^-$  can be written in another way, thus

$$J_n^- = \frac{2A}{\pi} \int_{\Omega(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) \left\{ \int_{\frac{|\vec{r}-\vec{r}'|}{t}}^{\infty} \frac{p^3 dp}{(2mkT_+)^2} e^{-\frac{p^2+2mU}{2mkT_+}} - \int_{\frac{|\vec{r}-\vec{r}'|}{t}}^{\infty} \frac{p^3 dp}{(2mkT_-)^2} e^{-\frac{p^2+2mU}{2mkT_-}} \right\}$$

or, after integrating with respect to p,

$$J_n^- = \frac{A}{\pi} \int_{\Omega(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) \left\{ \left( 1 + \frac{|\vec{r}-\vec{r}'|^2 m}{2kT_+ t^2} \right) e^{-\frac{|\vec{r}-\vec{r}'|^2 m}{2mkT_+ t^2} - \frac{U}{kT_+}} - \left( 1 + \frac{|\vec{r}-\vec{r}'|^2 m}{2kT_- t^2} \right) e^{-\frac{|\vec{r}-\vec{r}'|^2 m}{2mkT_- t^2} - \frac{U}{kT_-}} \right\}$$

when  $L^2 m/t^2 kT_+ \ll 1$

$$J_n^- = \frac{A}{\pi} (e^{-U/kT_+} - e^{-U/kT_-}) \int_{\Omega(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) + \frac{Am^2}{4\pi t^4} \left[ \frac{e^{-U/kT_-}}{(kT_-)^2} - \frac{e^{-U/kT_+}}{(kT_+)^2} \right] \times \int_{\Omega(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) |\vec{r}-\vec{r}'|^4 \quad (17)$$

Eq. (17) shows that  $J_n < 0$ , that is, that the surface beyond the limits of  $S_1$  is united by the molecules of the condensate.

The flow at any point of  $S_1$  can be found by using the formula

$$J_n^+ = A(e^{-U/kT_-} - e^{-U/kT_+}) + \frac{A}{\pi} \int_{\Omega(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \left( 1 + \frac{|\vec{r} - \vec{r}'|^2 m}{2kT_+ t^2} \right) e^{-\frac{|\vec{r} - \vec{r}'|^2 m}{2kT_+ t^2} - \frac{U}{kT_+}} - \left( 1 + \frac{|\vec{r} - \vec{r}'|^2 m}{2kT_- t^2} \right) e^{-\frac{|\vec{r} - \vec{r}'|^2 m}{2kT_- t^2} - \frac{U}{kT_-}} \right\}. \quad (17')$$

The second summand is small because of the smallness of  $1/\pi \int_{\Omega(\vec{r})} d\vec{\Omega}$  and  $(\vec{\Omega} n)$ , or, the smaller the section of the surface, the closer it is to a plane.

Eq. (17') shows that  $J_n^+ > 0$ . Some of the condensate is pumped from hot sites on the surface to cold. /729

Eqs. (17') and (17) remain valid so long as at least a few atomic layers of condensate remain on the section of the surface with temperature  $T_-$ . But  $n(\vec{r}, t)$  depends on arguments all its own, and this dependency can be found through Eq. (8). The function  $n_+(\vec{r}, t)$  remains as before.

Expressing the flow  $J_n$  in terms of  $n_-(\vec{r}, t)$ , and substituting it in Eq. (8), we obtain an integral equation for finding the function  $n_-(\vec{r}, t)$

$$\begin{aligned} \frac{n_-(\vec{r}, t)}{f(T_-)} = \frac{n_-}{f(T_-)} + \frac{1}{\pi} \int_0^t dt' \int_{\Omega(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \left( 1 + \frac{|\vec{r} - \vec{r}'|^2 m}{2kT_+ t'^2} \right) \times \\ \times e^{-\frac{|\vec{r} - \vec{r}'|^2 m}{2kT_+ t'^2}} A e^{-\frac{U}{kT_+}} + \frac{2}{\pi} \int_0^t dt' \int_{\Omega(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \int_{\frac{|\vec{r} - \vec{r}'| m}{t}}^{\infty} \frac{p^3 dp}{(2mkT_-)^3} \times \\ \times e^{-\frac{p^2}{2mkT_-}} n_-(\vec{r}', t' - \tau) - \int_0^t dt' n_-(\vec{r}, t') + \frac{n_-}{\pi} \int_0^t dt' \int_{\Omega(\vec{r})} d\vec{\Omega} (\vec{\Omega} n) \times \\ \times \left[ 1 - \left( 1 + \frac{|\vec{r} - \vec{r}'|^2 m}{2kT_- t'^2} \right) e^{-\frac{|\vec{r} - \vec{r}'|^2 m}{2kT_- t'^2}} \right]. \end{aligned}$$

If we introduce a new, unknown function  $\xi(\vec{r}, t) = n_-(\vec{r}, t) - n_-$ , and designate

$$t_{\pm} = \frac{|\vec{r} - \vec{r}'| m}{\sqrt{2mkT_{\pm}}},$$

the above equation can be rewritten in the form

$$\begin{aligned} \frac{\xi(\vec{r}, t)}{f(T_-)} + \int_0^t \xi(\vec{r}, t') dt' - \frac{1}{\pi} \int' d\vec{\Omega}(\vec{\Omega}n) \int_0^t dt' \xi(\vec{r}', t') \left[ 1 + \frac{t_-^2}{(t-t')^2} \right] e^{-\frac{t_-^2}{(t-t')^2}} = \\ = -\frac{1}{\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) \int_0^t dt' \left\{ n_- \left( 1 + \frac{t_-^2}{t'^2} \right) e^{-\frac{t_-^2}{t'^2}} - A e^{-\frac{U}{kT_+}} \left( 1 + \frac{t_+^2}{t'^2} \right) e^{-\frac{t_+^2}{t'^2}} \right\}. \end{aligned} \quad (18)$$

Completing the one-sided Laplace transform with respect to the variable  $t$  over both sides of Eq.(18), and designating the form of the function  $\xi(\vec{r}, t)$  by  $\xi(\vec{r}, s)$ , we obtain /730

$$\begin{aligned} \frac{1}{\pi} \int' d\vec{\Omega}(\vec{\Omega}n) [\xi(\vec{r}, s) - \xi(\vec{r}', s)] + \xi(\vec{r}, s) \frac{1}{\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) + \frac{s}{f(T_-)} \xi(\vec{r}, s) + \\ + \frac{s}{2\pi} \int' d\vec{\Omega}(\vec{\Omega}n) \xi(\vec{r}', s) t_- \zeta(t_- s) = -\frac{1}{\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) \frac{1}{s} (n_- - A e^{-\frac{U}{kT_+}}) - \\ - \frac{1}{2\pi} \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) \{ A e^{-\frac{U}{kT_+}} t_+ \zeta(t_+ s) - n_- t_- \zeta(t_- s) \}, \end{aligned} \quad (19)$$

$$\zeta(s) = 2 \int_0^{\infty} e^{-\tau s} \left\{ 1 - \left( 1 + \frac{1}{\tau^2} \right) e^{-\frac{1}{\tau^2}} \right\} d\tau,$$

$$\zeta(s) \approx \sqrt{\pi} - s + \frac{\sqrt{\pi}}{3} s^2 + \frac{s^3 \ln s}{6} \quad (s \ll 1). \quad (20)$$

The behavior of  $\xi(\vec{r}, t)$  for the case of long time intervals is of interest to us. It is determined by the asymptotic behavior of  $\xi(\vec{r}, s)$  for small  $s$  ( $s \ll 1$ ). Let us use the Eq. (20) expansion, and seek the solution of Eq. (19) in the form of the series

$$\xi(\vec{r}, s) = \frac{\xi_{-1}}{s} + \sum_{n=0}^{\infty} \xi_n(\vec{r}) s^n + \ln s \sum_{n=0}^{\infty} \tilde{\xi}_n(\vec{r}) s^n + \dots \quad (21)$$

Substituting Eq. (21) in Eq. (19), and grouping terms with identical powers of  $s$ , we obtain a chain of integral equations for finding the unknown functions  $\xi_{-1}, \xi_0, \xi_1, \dots, \tilde{\xi}_0, \tilde{\xi}_1$  etc. At the same time

$$\xi_{-1} = Ae^{-U/kT_+} - n_-$$

from whence it follows that

$$\lim_{t \rightarrow \infty} \xi(\vec{r}, t) = Ae^{-U/kT_+} - n_- \quad (22)$$

or

$$\lim_{t \rightarrow \infty} n_-(\vec{r}, t) = Ae^{-U/kT_+}$$

This result can be understood if it is recalled that in the steady-state case  $n(\vec{r}, t)$  should not depend on the coordinate, but rather on the section of the surface,  $S_1$ , where the temperature  $T = T_+$ ,  $n(\vec{r}, t) = Ae^{-\frac{U}{kT_+}}$  for any value of  $t$ , including  $t \rightarrow \infty$ .

Since

$$\sum_{n=0}^{\infty} \xi_n(\vec{r}) s^n$$

is a function that is regular at zero with respect to the variable  $s$ , applying it to the inverse transform

$$\sum_{n=0}^{\infty} \xi_n(\vec{r}, t) = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} \sum_{n=0}^{\infty} \xi_n(\vec{r}) s^n e^{st} ds,$$



we obtain a function that is at the very least decreasing exponentially with time (for long time intervals).

We are readily persuaded that  $\tilde{\xi}_0, \tilde{\xi}_1, \tilde{\xi}_2$  equal zero, and we obtain the following equation for  $\tilde{\xi}_3(\vec{r})$

$$\begin{aligned} \tilde{\xi}_3(\vec{r}) - \frac{1}{\pi} \int' d\vec{\Omega}(\vec{\Omega}n) \tilde{\xi}_3(\vec{r}') &= \frac{m^2}{48\pi} \left\{ \frac{n_-}{(kT_-)^2} - \frac{Ae^{-U/kT_+}}{(kT_+)^2} \right\} \times \\ \times \int_{\vec{\Omega}(\vec{r})} d\vec{\Omega}(\vec{\Omega}n) |\vec{r} - \vec{r}'|^4 - \frac{\xi_{-1}}{48\pi} \int' d\vec{\Omega}(\vec{\Omega}n) \frac{|\vec{r} - \vec{r}'|^4 m^2}{(kT_-)^2} \end{aligned} \quad (23)$$

The summand in the expression for  $\xi(\vec{r}, t)$ , corresponding to the term  $\tilde{\xi}_3(\vec{r})s^3$  in Eq. (21) proves to be

$$\tilde{\xi}_3(\vec{r}, t) = 3! \frac{1}{t^3} \tilde{\xi}_3(\vec{r}), \quad (24)$$

that is,

$$\xi(\vec{r}, t) \approx Ae^{-U/kT_+} - n_- + \frac{3!}{t^3} \tilde{\xi}_3(\vec{r}).$$

We must make certain assumptions with respect to the shape of the expanse, and that section of it,  $S_1$ , where the temperature changes from  $T_-$  to  $T_+$  in order to determine the function  $\tilde{\xi}_3(\vec{r})$ . Let us assume that the expanse is a sphere with radius  $R$ , and that  $S_1$  is the surface of a spherical segment corresponding to the polar angle  $\vartheta_0$ .

Let us select the origin of the spherical coordinates as the point  $\vec{r}$ . Then

$$d\vec{\Omega}(\vec{\Omega}n) = \sin \Theta \cos \Theta d\varphi.$$

If the origin is shifted to the center of the sphere, and if the corresponding polar angle is designated  $\vartheta'$ , obviously  $\vartheta' = 2\Theta$ , and

$$d\vec{\Omega}(\vec{\Omega}n) = \frac{1}{4} \sin \vartheta' d\vartheta' d\varphi = \frac{1}{4R^2} dS,$$

where  $dS$  is an element of the surface of the sphere. Now let us change the direction of the polar axis, causing it to coincide with the diameter passing through the center of the spherical segment, and let us once again integrate with respect to the angle, instead of with respect to the surface. Eq. (23) can be written

$$\tilde{\xi}_3(\vec{r}) - \frac{1}{4\pi} \int' d\Omega \tilde{\xi}_3(\vec{r}) = \frac{m^2}{48\pi} \frac{n_- - Ae^{-U/kT_+}}{4(kT_-)^2} \int d\Omega |\vec{r} - \vec{r}'|^4 -$$

$$- Ae^{-U/kT_+} \left[ \frac{1}{(kT_+)^2} - \frac{1}{(kT_-)^2} \right] \frac{m^2}{48\pi \cdot 4} \int_{S_1} d\Omega |\vec{r} - \vec{r}'|^4, \quad (25) \quad \angle 732$$

$$|\vec{r} - \vec{r}'|^4 = 4R^4 (1 - \vec{n}\vec{n}')^2, \text{ where } \vec{n} = \vec{r}/R, \vec{n}' = \vec{r}'/R$$

$\vec{n}\vec{n}' = \cos \vartheta \cos \vartheta' + \sin \vartheta \sin \vartheta' \cos (\varphi - \varphi')$ , here  $\vartheta, \varphi, \vartheta', \varphi'$ , are the polar and azimuth angles of the points  $\vec{r}$  and  $\vec{r}'$ .

Integration of the right side of Eq. (25) with respect to the angle  $\varphi'$

$$\int_0^{2\pi} d\varphi (1 - \vec{n}\vec{n}')^2 = 2\pi \left\{ \frac{3}{2} - \frac{1}{2} \cos^2 \vartheta - \frac{1}{2} \cos^2 \vartheta' - 2 \cos \vartheta \cos \vartheta' + \right. \\ \left. + \frac{3}{2} \cos^2 \vartheta \cos^2 \vartheta' \right\}.$$

$\tilde{\xi}_3(\vec{r})$  obviously is a function of  $\cos \vartheta$ . Designating  $\cos \vartheta = x$ ,  $\cos \vartheta' = x'$ , let us integrate both summands in the right side of Eq. (25) with respect to  $\vartheta'$ . We obtain

$$\tilde{\xi}_3(\vec{r}) - \frac{1}{2} \int_{-1}^{\alpha} \tilde{\xi}_3(x') dx' = \frac{m^2 R^4}{9(kT_-)^2} (n_- - Ae^{-U/kT_+}) - \\ - Ae^{-U/kT_+} \frac{m^2 R^4}{24} \left[ \frac{1}{(kT_+)^2} - \frac{1}{(kT_-)^2} \right] \left\{ \frac{4}{3} + (1 + \alpha) \left[ -\frac{\alpha}{6} - x + \frac{\alpha x^2}{2} \right] \right\} (1 - \alpha).$$

Here  $\alpha = \cos \vartheta_0$ .

The solution of this equation is

$$\begin{aligned} \tilde{\xi}_3(x) = & \frac{m^2 R^4}{9 \sin^2 \frac{\vartheta_0}{2}} \frac{n_- - A e^{-U/kT_+}}{(kT_-)^2} - \frac{m^2 R^4}{24} A e^{-U/kT_+} \left[ \frac{1}{(kT_+)^2} - \frac{1}{(kT_-)^2} \right] \left\{ \frac{8}{3} + \right. \\ & \left. + \sin^2 \vartheta_0 \left[ \cos^2 \frac{\vartheta_0}{2} - \frac{1}{6} \cos \vartheta_0 (1 + \cos \vartheta_0 + \cos^2 \vartheta_0) - x + \frac{1}{2} x^2 \cos \vartheta_0 \right] \right\}. \end{aligned}$$

What follows from the expression obtained for  $\tilde{\xi}_3(x)$  and from Eq. (24) is that the characteristic time of temperature relaxation for small  $\vartheta_0$ , that is, the time over which  $\xi(\vec{r}, t)$  approaches its limit, determined through Eq. (22), is proportional to  $(S/S_1)^{1/4}$ , where  $S$  is the entire surface of the expanse, and  $S_1$  is that part of it the temperature of which changes from  $T_-$  to  $T_+$ .

Since  $J_n \sim \partial n(\vec{r}, t) / \partial t$ , and for long time intervals  $n \sim 1/t^m$  ( $m$  equals three, or four),  $J_n \sim 1/t^{m+1}$ . Thus, the full flow tends to zero more rapidly than does  $n(\vec{r}, t)$  to its limit, so the relaxation time must be considered the characteristic time for the establishment of a steady-state flow of desorbing particles. [73]

The results show that the flow of particles being set up is determined by the lowest temperature of the cold surface. The time required to establish the steady-state desorption flow (the temperature relaxation time) is proportional to the square root of the fourth power of the ratio of the entire area of the internal surface of the vacuum chamber to its cold part.

Let us emphasize the fact that the results obtained are valid for surfaces satisfying the condition of convexity, and which have one characteristic dimension. Moreover, we made use of the assumptions that any particle flying in a direction toward the surface settles on that surface (is adsorbed), and is "thermalized." But it should "settle" on this surface for some time (of the order of  $\tau_0$ ) for this to occur. This does take place, evidently, at temperatures near the condensation temperature. The reflectance must be taken as other than zero at high temperatures, and this greatly complicates the problem.

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